Stability of CO₂ Fluid in Eclogitic Mantle Lithosphere: Thermodynamic Calculations

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Abstract: Findings of solid and liquefied CO₂ in diamonds from kimberlites and placers have indicated its presence in the form of a fluid phase in the Earth’s mantle at depths of 150–250 km. However, this is inconsistent with the results of experiments and existing thermodynamic calculations. To clarify this, we carried out thermodynamic modeling of garnet–CO₂ and bimineral eclogite–CO₂ systems using the Perple_X v. 7.1.3 software package, which establishes the most thermodynamically favorable assemblages for a given bulk composition of the system, unlike previous calculations, for which the phase relationships were simply assumed. The key difference between our results and previously known data is the presence of a region of partial carbonation. In this region, the garnet and clinopyroxene of the new compositions, CO₂ fluid, carbonates, kyanite, and coesite are in equilibrium. The calculations revealed that unlike endmember systems (pyrope–CO₂ and diopside–CO₂) in the eclogite–CO₂ system, the carbonation and decarbonation lines do not coincide, and the Grt+Cpx+CO₂ and Carb+Ky+Coe+Cpx fields are separated by the Grt+Cpx+CO₂+Carb+Ky+Coe region, which extends to pressures exceeding 4.3–6.0 GPa at 1050–1200 °C. This should extend the CO₂ stability field in the eclogitic mantle to lower temperatures. Yet, owing to the short CO₂ supply in the real mantle, the CO₂ fluid should be completely spent on the carbonation of eclogite just below the eclogite + CO₂ field. Thus, according to the obtained results, the CO₂ fluid is stable in the eclogitic mantle in the diamond stability field at temperatures exceeding 1250 °C and pressures of 5–6 GPa.

Keywords: CO₂ fluid; Earth’s mantle; phase relations; thermodynamic calculations

1. Introduction

CO₂ is an important volatile component responsible for the partial melting and generation of magmas such as kimberlites and carbonatites in the Earth’s upper mantle [1]. Unlike subducted H₂O/OH⁻, which is mostly lost at subarc depths [2–4], CO₂ as carbonates sinks deeper into the mantle [5] and is extracted in the form of a carbonate melt [6] or CO₂ fluid during the progressive warming of a stagnant slab [7]. Findings of inclusions saturated with volatile components in the eclogites of the diamond facies of metamorphism are rare, and all of them are confined to diamond crystals. Shatsky et al. [8] reported numerous CaCO₃ microinclusions in diamonds from an eclogite xenolith from the Udachnaya pipe (Russia). Zedgenizov et al. [9] described findings of K-rich low-Mg chloride–carbonate microinclusions in diamonds with a fibrous internal structure from an eclogite xenolith of the same pipe.

Considering the findings of liquefied CO₂ in minerals associated with the diamond deposits reported by Roedder [10], Kennedy and Nordlie [11] suggested that CO₂ was responsible for the diamonds’ formation. Later, CO₂ inclusions were indeed discovered in the diamonds themselves. These were submicron solid inclusions under residual levels of pressure up to 5 GPa [12–14] and optically visible (10–70 µm) liquid inclusions in healed fractures mixed with N₂ and hydrocarbons [15,16]. The findings of these inclusions may indicate the presence of CO₂ fluid in the crystallization medium of some diamonds.
Furthermore, the crystallization of diamonds in CO₂ fluid was realized in experiments under P-T conditions close to those for natural diamond formation [17]. However, according to experimental data, the stability of CO₂ in the most common ultramafic mantle is limited by carbonation reactions involving olivine, which occur at pressures of 1.0–2.5 GPa [18,19].

It should also be noted that mineral inclusions found in CO₂-bearing diamonds belong to the eclogite suite [13,20,21]. Meanwhile, some diamonds that entrapped solid CO₂ at higher pressures may have formed under different conditions—such as based on the redox freezing mechanism [22]. Experiments show that the stability field of CO₂ fluid with minerals of the eclogitic suite in the pyrope–CO₂ and diopside–CO₂ systems extends to higher pressures compared to the peridotite mantle but still does not reach the diamond stability field [23–27]. Nevertheless, the studied systems do not adequately model the compositions of eclogite garnets and clinopyroxenes, which are known to be represented by pyrope–almandine–grossular solid solutions and omphacite (diopside–jadeite solid solution), respectively. Using thermodynamic calculations, Knoche et al. [23] showed that the dilution of the diopside component in clinopyroxene and the pyrope component in garnet shifts the carbonation reaction boundaries to higher pressures. These calculations were verified by experiments with clinopyroxenes of the diopside–jadeite series [28]. The results showed that jadeite does not undergo a carbonation reaction, so clinopyroxene with a high jadeite content coexists with CO₂ to at least 6–6.5 GPa and 1050–1100 °C. In the case of garnet, experimentally identified trends are not so obvious. The stability field of the Grt+CO₂ assemblage in the Prp₃₅Alm₄₀Grs₅₀–CO₂ system extends to lower temperatures relative to those of the Prp–CO₂ system at a pressure of 3 GPa but remains unchanged at 6.3 and 7.5 GPa [29]. A similar trend is observed in the Prp₃₀Alm₇₀–CO₂ system [25].

Previous thermodynamic calculations [23,25,30] assume that regardless of the composition of the solid solution outside the Grt+CO₂ field, garnet completely reacts with CO₂ to produce kyanite, coesite, and carbonate as shown below:

\[
(Ca,Mg,Fe)₃Al₂Si₃O₈ \text{(Prp)} + 3CO₂ \text{(fluid)} = 3(Ca,Mg,Fe)CO₃ \text{(Carb)} + Al₂SiO₅ \text{(Ky)} + 2SiO₂ \text{(Qz/Coe)} \quad (1)
\]

Yet, the experiments reveal the garnet crystallization outside the Grt+CO₂ stability field, wherein the cation composition of the newly formed garnet differs significantly from the bulk composition of the Grt–CO₂ system [25,29,31]. These may be associated either with sluggish kinetics or more complex phase relations.

To clarify this in the present study, we carried out thermodynamic modeling of the pyrope–almandine–grossular–CO₂ system using the Perple_X v. 7.1.3 software package [32,33], which establishes the most thermodynamically favorable assemblage for a given bulk composition of a system, unlike previous calculations, in which the phase relationships were simply assumed. Finally, we also performed thermodynamic calculations for the bimineral eclogite–CO₂ system.

### 2. Methods

**T-X diagrams and P-T pseudo-sections** were calculated using the Perple_X v. 7.1.3 software package [32] in the range of 900–1500 °C and 3–6 GPa. The calculations were carried out for the CaO-MgO-FeO-Al₂O₃-SiO₂-CO₂ system (+Na₂O when modeling eclogite) with component ratios corresponding to reagents in carbonation reactions taken in equal proportions (i.e., Grt+3CO₂ and Cpx+2CO₂). The calculations were performed for the following subsystems: (1) Prp–Grs+CO₂, (2) Prp–Alm₃₀Grs₅₀+CO₂, and Prp₅₀Grs₅₀Alm₅₀+Di₇₀Jd₃₀+5CO₂. For the mineral component, the database from Holland and Powell [34] was used with compatible solid solution models: the Gt(HGP) model for garnet solution [35]; Omph(HP) for a clinopyroxene solution [11,36], cCm(EF) for a ternary solution of calcite–magnesite–siderite carbonates, and LiQ(EF) for a carbonate melt [37]. Perple_X v. 7.1.3 has 7 equations of state (EOS) for CO₂ fluid. In this study, we used compensated Redlich–Kwong (CORK) EOS from Holland and Powell [38] who extended the modified Redlich–Kwong (MRK) EOS to 5 GPa and 1600 °C. Calculations were performed with the default resolution values since they did not cause significant distortions in the diagrams. Minimization was conducted on a 4-level
grid with 40 × 40 nodes, which had a spacing of 9.6 MPa (0.0096 GPa) at 1.9 °C and with 0.3 mol%. The equations of states of a ternary solution of calcite–magnesite–siderite carbonates oCcM(EF) and a carbonate melt LIQ(EF) are both based on the experiments at 3.5 GPa in CaCO$_3$-MgCO$_3$-FeCO$_3$ system [37].

There are several studies on phase relations along the pyrope–grossular join [39–43]. The existence of a miscibility gap was reported in all studies, though its position varies. Immiscibility is accompanied by the formation of clinopyroxene and corundum [39,42], which corresponds to the CaSiO$_3$-MgSiO$_3$-Al$_2$O$_3$ ternary section. The solid solution model for garnet was chosen based on the results of Surkov and Gartvich [42]. According to their data at 3.0 GPa above 1000 °C, the miscibility gap of garnet appears, and clinopyroxene with the diopside–Ca–chermakite composition forms. The composition of omphacite was modeled by the diopside–jadeite–hedenbergite system as CaMgSi$_2$O$_6$-NaAlSi$_2$O$_6$-CaFeSi$_2$O$_6$.

The dis(EF) model of Franzolin et al. [37] does not account for the formation of Dol and Ank phases with variable compositions, which is inconsistent with experimental results for binary and ternary carbonates [44–46]. The key difference from the original model is the absence of a miscibility gap in the region of compositions with Cal# > 50 near the solidus line, which significantly affects the topology of the diagrams. In this regard, the oCcM(EF) model parameters for carbonate solid solutions were adjusted so that the calculated T-X diagrams of CaCO$_3$-MgCO$_3$ were as close as possible to the experimentally determined ones [45]. The W parameters of the oCcM(EF) model for the Mgs–Cal compound were slightly modified to expand the CaLss region and move Cal+Arg region away from the solidus line in accordance with the experimental results of Shatskiy et al. [45]. Modification was made by trial-and-error method. In many other parameters, it is still the original oCcM(EF) model. The selected parameters of chemical interaction have the following values: $W$(Mgs, Cal) = 25,000 J/mol, $W$(Cal, Dol) = 8200 J/mol, and $W$(Mgs, Dol) = 15,500 J/mol.

The lack of reliable models simulating mantle carbonatite melts casts doubt on the validity of calculated suprasolidus phase relationships. Therefore, phase fields located above the experimentally inferred solidus of the silicate–CO$_2$ systems should be considered imaginary. The problem is discussed in detail in the discussion section.

3. Results

3.1. Pyrope–Grossular

In the beginning, we calculated the pyrope–grossular–CO$_2$ system, which has the greatest deviations from the ideal solution. The results are summarized in the isobaric T-X diagrams given in Figure 1. There are more than two phases in the phase fields because the isobaric T-X diagrams are pseudo-binary systems.

As can be seen, the Grt+CO$_2$ fields (shown in dark gray) have a complex shape and occupy limited areas in the T-X space. On the pyrope side, the Grt+CO$_2$ field is much wider than that on the grossular side. Even at 6 GPa, at which the mutual solubility of garnets is not limited, the Grt+CO$_2$ field does not go beyond Ca#60 on the pyrope side and completely disappears on the grossular side. At higher bulk Ca#, partial melting occurs. Thus, at higher temperatures and Ca#, the formation of a carbonate melt turns out to be thermodynamically more favorable than the transition to the Grt+CO$_2$ assemblage. It should be noted that the melt model used in the present study does not take into account the possible influence of CO$_2$ on the melting of the system. See the discussion section for the details.
In the low-temperature part of the \( T \)-\( X \) diagrams, the Carb+Ky+Coe fields appear (the unshaded fields in Figure 1). Their shape follows that of the corresponding fields on the \( \text{CaCO}_3 \)-\( \text{MgCO}_3 \) \( T \)-\( X \) diagrams. As can be seen, the Carb+Ky+Coe fields do not have a common boundary with the Grt+\( \text{CO}_2 \) fields, only point contacts at \( \text{Ca}# = 20, 30, \) and 100. For the remaining compositions, the Carb+Ky+Coe and Grt+\( \text{CO}_2 \) fields are separated by the Grt+\( \text{CO}_2 \)+\( \text{Cal}+\text{Ky}+\text{Coe} \)/Cpx fields.

The upper part of the \( T \)-\( X \) diagrams (Figure 1a,b) contains regions describing phase equilibria involving silicate melt, garnet, and pyroxene. Since they are not involved in carbonation reactions and have no effect on them, they are not considered in this study and are left unlabeled.

Unlike pyrope, the garnets of the pyrope–grossular series do not react with \( \text{CO}_2 \) via reaction 1. Figure 2 shows the \( P \)-\( T \) pseudo-sections calculated for \( \text{Ca}# = 20, 40, 50, 60, \) and 80. There is a low-temperature boundary of the Grt+\( \text{CO}_2 \) field (the orange lines in Figure 2b–f), below which garnet reacts with \( \text{CO}_2 \) to produce Grt+\( \text{CO}_2 \)+\( \text{Cal}+\text{Ky}+\text{Coe} \) and the newly formed garnet has a distinct composition. Moreover, there is a boundary below which the \( \text{CO}_2 \) fluid completely reacts with the garnet (the blue lines in Figure 2b–f).
As can be seen, the yielding a change in the clapeyron slope (Figure 2d,e). At lower pressures and higher temperatures, the Cpx+Grt+CO$_2$+Cal+Ky/Coe assemblage is replaced with the Cpx+CO$_2$+Cal+Ky/Coe assemblage (fields 5 and 5* in Figure 2d,e), which is represented by the Grt+CO$_2$, Grt+CO$_2$+Cal+Ky/Coe, and Grt+CO$_2$+Cal+Ky/Coe assemblage (fields 5 and 5* in Figure 2d,e). Below 4.5 GPa and Ca# > 50, the Grt+CO$_2$+Cal+Ky/Coe assemblage is replaced with the Cpx+CO$_2$+Cal+Ky/Coe assemblage (fields 5 and 5* in Figure 2d,e), yielding a change in the clapeyron slope (Figure 2d,e). At lower pressures and higher temperatures, the Cpx+Grt+CO$_2$+Cal+Ky/Coe assemblage stabilizes (fields 4 and 4* in Figure 2d,e).

3.2. Pyrope–Almandine–Grossular

The calculations were performed for the Prp–Alm$_{50}$Grs$_{50}$ section, which is the most representative for eclogites (Figure 3). The results of the calculations are shown in Figure 4. As can be seen, the T-X space contains three regions: Grt+CO$_2$, Grt+CO$_2$+Carb+Ky+Coe (partial carbonation region), and Carb+Ky+Coe (full carbonation region). The last two regions are divided into several fields owing to the diversity of carbonates in the CaCO$_3$-MgCO$_3$-FeCO$_3$ join. The Grt+CO$_2$ region appears at high temperatures and is continuous over the entire range of compositions. It is separated from the Carb+Ky+Coe region by the Grt+CO$_2$+Carb+Ky+Coe region (Figure 4a–c). Thus, for the section considered, no garnet would react with CO$_2$ to produce the Carb+Ky+Coe assemblage directly.
During the partial carbonation, iron and, to a lesser extent, magnesium accumulate in the garnet, while the calcium actively passes into the carbonate phase. The composition of the garnet in the field of partial carbonation differs from the composition of the garnet in the field of partial carbonation with decreasing temperature.

On T-X diagrams, the lower boundary of the Grt+CO₂ field (partial carbonation line) extends from the Prp to the Grs₅₀Alm₅₀ side through a minimum temperature situated around (Ca+Fe)# 40–50. The maximum variations in temperature at a constant pressure of the partial carbonation line do not exceed 40–80 °C (Figure 4a–c). In contrast, the upper margin of the Carb+Ky+Coe assemblage (full carbonation line) continuously decreases by 200–250 °C along the Prp–Grs₅₀Alm₅₀ section. This expands the field of partial carbonation in the direction from the Prp toward the Grs₅₀Alm₅₀ (the light-gray area in Figure 4a–c).

For the Prp₅₀Grs₅₀Alm₅₀ composition, the P-T pseudo-section was calculated (Figure 4d). As can be seen, the lines of partial and full carbonation of the Prp₅₀Grs₅₀Alm₅₀ solid solution are lower in temperature than those of the pyrope carbonation line (Prp+CO₂) but higher than those of the almandine carbonation line (Alm+CO₂).

The composition of the garnet in the field of partial carbonation differs from the composition of the garnet in the Grt+CO₂ field, where it corresponds to the bulk composition of the system. The garnet in the partial carbonation field is richer in the almandine component, whose content increases with decreasing temperature (Figure 3).

Our calculations predict an increased CO₂ stability with the three-component garnet due to the almandine component, although it is lower than that of pure almandine. In this case, for all of the garnet compositions in the considered section, a region of partial carbonation is observed, in which the garnet and the carbonate phase coexist (Figure 4a–c). During the partial carbonation, iron and, to a lesser extent, magnesium accumulate in the garnet, while the calcium actively passes into the carbonate phase.

3.3. Eclogite–CO₂

Since at high pressures not only garnet, but also clinopyroxene can react with CO₂, it is of interest to study the garnet–clinopyroxene–CO₂ system to clarify the region of stability of CO₂ in the eclogite mantle. The main components of clinopyroxene in eclogites are diopside and jadeite. An experimental study of the reaction of diopside–jadeite solid solutions with CO₂ showed that the jadeite component does not react with CO₂ up to at least 950 °C at 6 GPa [28]. Therefore, the CaCO₃-MgCO₃-FeCO₃ ternary solid solution model was employed for calculations of the carbonate portion, while the Na₂CO₃ component was ignored. However, at high temperatures, a carbonate melt is formed, which also

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Figure 3. Diagram of the composition of garnets from eclogites [47]. The grey area shows the field of garnets from eclogite xenoliths from Udachnaya kimberlite pipe (Yakutia, Russia). The eclogitic garnets of Groups A, B, and C according to the classification of Taylor and Neal (Taylor and Neal, 1989). The black solid line shows the cross-section taken to calculate the T-X diagrams. The red triangle is the starting composition of Prp₅₀Grs₅₀Alm₅₀ garnet. The dotted lines with the arrow show the change in the composition of garnet in the field of partial carbonation with decreasing temperature.
contains dissolved Na₂CO₃. Unfortunately, at present, there is no model for such a melt in the Perple_X v. 7.1.3 database. Despite this, it was decided to carry out calculations with existing models of solid solutions to identify the possible interactions between solid phases. To reduce possible distortions due to differences in the composition of the melt, clinopyroxene with a low jadeite content was used for our calculations. Since the previously discussed garnet falls into Group B according to the classification of Taylor and Neal [48], the pyroxene was taken from the same group. An equimolar mixture of Prp₅₀Grs₂₅Alm₂₅ garnet and Di₇₀Jd₃₀ pyroxene was employed to model the eclogite. CO₂ was added in an amount equal to the number of cations in the system. The composition of the system can be approximated as follows: Prp₅₀Grs₂₅Alm₂₅+Di₇₀Jd₃₀+5CO₂.

**Figure 4.** Phase relations in the Prp–Grs₂₅Alm₂₅+3CO₂ system. T-X diagrams at 3 GPa (a), 4.5 GPa (b), and 6 GPa (c). P-T diagram for the Prp₅₀Grs₂₅Alm₂₅+3CO₂ bulk composition (d). The dotted lines show the equilibrium lines for the reactions of end-member phase components with CO₂. The orange line is the decarbonation reaction. The blue line is the partial decarbonation reaction. The garnet–CO₂ fields are highlighted in dark grey. Fields of partial carbonation are shaded in light gray. Unfilled areas are complete carbonation fields.

As the eclogite carbonates, the clinopyroxene composition shifts to be more jadeitic. The presence of the jadeite component extends the stability range of clinopyroxene to at least 900 °C and 6 GPa (Figure 5a). At these P-T conditions, the jadeite component predominates in the clinopyroxene composition. As the temperature increases, the diopside content increases (Figure 6b), even though pure diopside at these conditions is unstable.
with CO₂ (Figure 5a). Thus, the Carb+Ky+Coe+Cpx+CO₂ assemblage forms as a result of the full carbonation of eclogite. The clinopyroxene fraction in this assemblage does not exceed 5 mol% (Figure 5b).

**Figure 5.** Phase relations in the Prp₅₀/Grs₂₅/Alm₂₅+Dj₇₀/Jd₃₀+5CO₂ system. (a) P-T diagram. The dotted lines show the equilibrium lines for the reactions of end-member phase components with CO₂. The orange line is the eclogite partial carbonation line. The blue line is the eclogite carbonation line. Fields of partial carbonation of garnet are highlighted in gray. The eclogite–CO₂ field is highlighted in dark gray. (b) Mole fractions of garnet (dash-dotted line) and clinopyroxene (solid line) as a function of temperature at 4.5 GPa.

**Figure 6.** Calculated garnet (a) and clinopyroxene (b) compositions in the Prp₅₀/Grs₂₅/Alm₂₅+Dj₇₀/Jd₃₀+5CO₂ system at 3, 4.5, and 6 GPa compared with the eclogitic garnet and clinopyroxene of Group A, B, and C, according to the classifications of Coleman et al. [49] and Taylor and Neal [48], respectively. The ranges of eclogitic garnet compositions (light-grey area) and omphacite (light-grey area) correspond to those of Taylor et al. [47]. The dotted and solid lines with the arrow show the change in the composition of garnet (a) and clinopyroxene (b) in the field of partial carbonation and the eclogite–CO₂ field, respectively, with decreasing temperature. The red triangles are initial compositions of garnet and clinopyroxene.

In the field of the partial carbonation of eclogite, both pyroxene and garnet are present (the light-grey field in Figure 5a). Their fraction increases sharply with increasing temperature (Figure 5b). The region of partial carbonation itself is somewhat wider than that calculated for the Prp₅₀/Grs₂₅/Alm₂₅+3CO₂ system due to the deviation in the upper boundary—the eclogite carbonation line—towards higher temperatures. It can be assumed that these deviations are caused by the reaction of clinopyroxene with CO₂ since garnet has an almost uniform composition and fraction above field 1 (Figures 5b and 6a), which coincides with the carbonation
line of the garnet Prp$_{50}$Gr$_{25}$Al$_{25}$ (Figure 5a). The mole fraction of the garnet in the system shows an inflection during the transition from field 1 to field 2 (Figure 5b).

The composition of garnet in the region of partial carbonation changes from more almandine to more pyrope with increasing temperature (Figure 6a). The grossular content increases with pressure and remains almost unchanged with temperature (Figure 5b). The diopside content (MgO/Na$_2$O ratio) in clinopyroxene increases with increasing temperature. The component ratios shift because of the re-equilibration with garnet, resulting in differences in clinopyroxene compositions at different pressures (Figure 6b). The iron content in clinopyroxene remains at approximately the same level of about 4 wt% FeO or 12 mol% heddergite.

According to the calculation results, when clinopyroxene and garnet are present together, they react with CO$_2$ in parallel with the compositions re-equilibrating among themselves. The composition of garnet and clinopyroxene in the Grt+Cpx+CO$_2$ field is somewhat different from the initially specified one. Garnet contains more pyrope (55–60 mol%) and significantly less grossular (about 15–20 mol%) due to the formation of the Ca-herzolite component in clinopyroxene (Figure 6). The lower margin of the Grt+Cpx+CO$_2$ field almost coincides with the pyrope carbonation reaction. At 5.5 GPa, it abuts the solidus line of the system (Figure 5a). The line of carbonation of the eclogite lies significantly below the line of the reaction of the diopside with CO$_2$, while the diopside here is the only component of clinopyroxene participating in the reaction (Figure 5a).

The lower boundary of the eclogite + CO$_2$ field intersects the graphite-to-diamond transition line at 4.9 GPa and 1250 °C (Figure 7). As can be seen, the overlap of the Ec+Cpx+CO$_2$ field and $P$-$T$ conditions for the formation of lithospheric diamonds occurs in a very narrow region corresponding to a geotherm of 42 mW/m$^2$ and depths of $\geq$160 km. At the same time, the lower boundary of the field of carbonated eclogite + CO$_2$ crosses the graphite-to-diamond transition near 4.3 GPa and 1050 °C, which corresponds to a heat flow of 39 mW/m$^2$ (the pink field in Figure 7). At a heat flow of 37 mW/m$^2$ in the considered pressure range, only the Carb+Ky+Coe+Cpx+CO$_2$ assemblage is stable (Figure 7).

Since the melt model does not fully describe the melting reaction, the solidus line of the eclogite–CO$_2$ system from Yaxley and Brey [5] was taken as the upper boundary of the Ec+Cpx+CO$_2$ field (green line in Figure 7). The calculated subsolidus assemblage is represented by Gr+Cpx+Cal-Dol±Coe. At pressures > 5.5 GPa, the calculated solidus (Figure 5a) continues the experimental solidus reported by Yaxley and Brey [5] for the Grt+Cpx+Cal-Dol±Coe assemblage (Figure 7).

![Figure 7](image_url)

**Figure 7.** Phase relationships in the system of eclogite–CO$_2$ according to thermodynamic calculations. The $P$-$T$ fields of CO$_2$ fluid stability in the eclogitic suite and partial carbonation of eclogite are shown in grey and pink, respectively. The green line is the solidus of the system of eclogite–CO$_2$ taken from Yaxley and Brey [5]. Gr/Dia—graphite-to-diamond transition [50]. Dash-dotted lines—continental geotherms (37, 40, and 43 mW/m$^2$) after Hasterok and Chapman [51]. Mantle adiabat (light grey) is taken from [52]. The dotted line delimits the $P$-$T$ range of lithospheric diamond formation.
4. Discussion

The key difference between our results and previously known data is the presence of the so-called region of partial carbonation. In this region, the silicates, CO$_2$ fluid, carbonates, kyanite, and coesite are in equilibrium. The width of the field of partial carbonation of the eclogite varies from 70 to 150 °C depending on the bulk composition and pressure (Figures 4 and 5). The width of this field is comparable to or exceeds the typical temperature step of multi-anvil experiments (50–100 °C). This means that a similar assemblage should have been observed earlier in experiments. Indeed, in the work of Bataleva et al. [25] on the Prp$_{35}$Alm$_{40}$Grs$_{25}$-CO$_2$ system, the resulting samples contained garnet, carbonates (dolomite, ankerite, Fe–magnesite) kyanite, and coesite. When analyzing the data, the authors of the work proceeded from the results for the pyrope–CO$_2$ system, for which only two stable assemblages were possible—Prp+CO$_2$ and Mgs+Ky+Coe. Accordingly, since the starting material was a carbonate–oxide mixture, the appearance of garnet in it was interpreted as a transition to the Grt+CO$_2$ stability field. According to our calculations, these observations [25,29] should be interpreted as a transition to the Grt+CO$_2$+Carb+Ky+Coe field. This hypothesis is supported by the small difference in the position of the lines obtained for the Mgs+Ky+Coe and Dol+Ky+Coe mixtures, as well as the nature of the shift in the compositions of the resulting garnets from the initial Ca/Mg/Fe ratio. From the dolomite with Mgs$_{50}$Cal$_{50}$, the garnet Prp$_{83}$Grs$_{17}$ was formed, i.e., a more pyrope-rich garnet, while from the ankerite Mgs$_{37}$Cal$_{47}$Sid$_{15}$ Prp$_{35}$Grs$_{25}$Alm$_{40}$ was formed, i.e., a more ferrous garnet with less calcium. Similar compositional shifts were observed in the region of partial carbonation. In addition, according to our calculations, in this region, the composition of the garnet depends on the pressure, which was also observed in the work of Bataleva et al. [25].

According to our calculations, for a Grt–CO$_2$ system with the same bulk composition, the carbonation and decarbonation lines do not coincide. This is an important feature of the CO$_2$ reaction with the Prp–Alm–Grs solid solution since the Grt+CO$_2$ and Carb+Ky+Coe fields are separated by the Grt+CO$_2$+Carb+Ky+Coe field.

Although thermodynamic calculations were used in all previous works [23,25,29], their results did not reveal the presence of a region of partial carbonation. This discrepancy is caused by the difference in approaches for calculating reactions of solid solutions. The earlier studies employed a fixed composition of the solid solution, specified through the values of the activities of the components. Knoche et al. [23] and Vinogradova et al. [30] calculated lines for each of the components, taking into account the changed activity using the TWQ program of Berman [53] version 1.02, JUN92.GSC mineral data, and the THERMOCALC program of Holland and Powell [36] version 3.45, respectively. Bataleva et al. [25] calculated the general position of the reaction line using the approach reported in [53,54], but the reaction is generated based on the reaction equations of the end-member phase components. Therefore, both algorithms do not imply the possibility of forming a stable assemblage other than Carb+Ky+Coe and Grt+CO$_2$.

The Perple_X v. 7.1.3 software package differs in that the user specifies the bulk composition of the system, and then the algorithms generate a set of possible solid solutions with a certain compositional step. From the resulting set of phases, the thermodynamically most favorable assemblage at a specific point in the diagram is identified. Thus, the program calculates the phase composition over the entire field of the diagram with a given grid and then adds boundaries between points of different compositions. With this approach, the reaction equations of the end-member phase components and their solutions do not appear in any way in the calculations, but they are determined later based on the results. Only the boundaries of the phase transitions between different polymorphs of the same substance are fixed.

The result of calculations in Perple_X v. 7.1.3 is strongly influenced by the list of solution models that the user selects. For example, if we exclude the clinopyroxene model when calculating the Prp–Grs-CO$_2$ diagram (Figure 2), the result will show a continuous solution for the garnet at all pressures, as was the case in the Prp–Grs–Alm–CO$_2$ system.
was quenched at 5.7–6.3 GPa and 1200–1600° with graphite/diamond under reduced conditions controlled by an Fe-FeO buffer, which (Figure 4). The area of partial carbonation will remain. The rationale for our choice of pattern for the program predicts the coexistence of CO₂ and phase diagrams. It was experimentally shown that CO₂ will dissolve in the carbonate melt, and its solubility increases with increasing pressure [55]. In this case, the melting point of the carbonate–CO₂ mixture is lower than that of the original carbonate. A similar effect can be expected in the system we are studying in the current paper, especially for the areas for which the program predicts the coexistence of CO₂ and carbonate melts. This assumption is confirmed by the results of experiments in Di-CO₂ and Di-Jd–CO₂ systems [26,28], which showed a decrease in the melting temperature compared to carbonate–silicate systems without an excess of CO₂ [56]. In addition, the Di-Jd–CO₂ system has a lower melting point compared to that of diopside–CO₂.

For Ca and Mg carbonates, it has been experimentally shown that CO₂ will dissolve in the carbonate melt, and its solubility increases with increasing pressure [55]. In this case, the melting point of the carbonate–CO₂ mixture is lower than that of the original carbonate. A similar effect can be expected in the system we are studying in the current paper, especially for the areas for which the program predicts the coexistence of CO₂ and carbonate melts. This assumption is confirmed by the results of experiments in Di-CO₂ and Di-Jd–CO₂ systems [26,28], which showed a decrease in the melting temperature compared to carbonate–silicate systems without an excess of CO₂ [56]. In addition, the Di-Jd–CO₂ system has a lower melting point compared to that of diopside–CO₂.

In addition, the CO₂ fluid itself can act as a solvent, as evidenced by the experimental results presented in the article by Novoselov et al. [31]. According to the authors, CO₂ partially dissolves garnet in the absence of carbonation, and predominantly Ca passes into the fluid. This process, firstly, will change the composition of garnet even within the Grt+CO₂ region, and secondly, it will reduce the activity of CO₂ itself, which will affect the position of the region boundaries on phase diagrams.

Summarizing the above, we can conclude that diagrams for real systems may have a slightly different position of the boundaries, different from the calculated one, due to possible phase mixing that is not taken into account by the models. Since it seems extremely difficult to take into account all of these effects in calculations, it is necessary to conduct an experimental study of the phase relationships in the garnet–CO₂ and eclogite–CO₂ systems, taking into account the discovered features.

Due to clinopyroxene, the temperature of the onset of carbonation of eclogite is significantly higher than that of garnet, which shifts the eclogite + CO₂ field in the P-T stability field of diamond to temperatures exceeding 1250 °C (Figure 7). Although the eclogite–carbonate–CO₂ assemblage is stable at lower temperatures, under conditions of CO₂ deficiency, the CO₂ fluid will be completely consumed for the eclogite carbonation just below the eclogite + CO₂ field stability.

CO₂ fluid is stable under oxidized conditions corresponding to the CCO buffer. Sokol et al. [57,58] performed the chromatographic analysis of the C-O-H fluid coexisting with graphite/diamond under reduced conditions controlled by an Fe-FeO buffer, which was quenched at 5.7–6.3 GPa and 1200–1600 °C. Their results show that the quenched fluid varies from H₂O >> H₂ > CH₄ (at f/O₂ value somewhat lower than the ”water maximum”) to H₂ > CH₄ > (C₂H₄ + C₂H₆) > C₃H₈ (in the C–H system). These experiments indicate that the sequential reduction in CO₂-bearing fluid yields the precipitation of diamond and changes the fluid composition to H₂- and CH₄-bearing H₂O and finally to CH₄-H₂ fluid. This agrees well with the Raman spectra from the Fe-Ni-C-S melt inclusions in large gem diamonds, which revealed the presence of methane and hydrogen [59]. Thus, diamond, Fe-Ni-S-C melt, and methane are the main carbon hosts in the mantle under reduced conditions, while CO does not form under a high pressure.

Findings of CO₂ fluid in diamonds [20,21] may not be accidental. CO₂ fluid can be formed as a result of the metamorphic degassing of oceanic plates when they are heated during low-angle subduction beneath the continental lithospheric mantle [7,60,61]. It was experimentally shown that CO₂ fluid could be responsible for diamond crystallization as a solvent catalyst [62,63] and carbon source [64]. Most of the mineral inclusions found in CO₂-bearing diamonds belong to the eclogitic suite [13,20,21]. Indeed, our results show that, in contrast to ultramafic rocks, CO₂ fluid could be stable in the eclogitic suite under P-T conditions of lithospheric diamond formation at temperatures exceeding 1250 °C (Figure 7). The penetration of CO₂ fluid into the eclogitic mantle should be accompanied by partial
carbonation, a decrease in the pyrope component in garnet, and an increase in the jadeite component in clinopyroxene, shifting the composition of the eclogite towards Group C.

5. Conclusions

Based on the results of our thermodynamic calculations in the Perple_X v. 7.1.3 software package for the systems of Prp–Grs+3CO$_2$, Prp–Alm$_{50}$Grs$_{50}$+3CO$_2$, and Prp$_{50}$Grs$_{25}$Alm$_{25}$+Di$_{70}$Jd$_{30}$+5CO$_2$ conducted using the ranges of 3–6 GPa and 900–1500 °C, the following conclusions can be drawn:

1. In the Prp–Grs+3CO$_2$ system, from the low-pressure and high-temperature side, the Grt+CO$_2$ field is limited by the reaction of the partial decomposition of garnet:

\[
\text{Grt} \rightarrow \text{Cpx} \pm \text{Grt}_{\text{new}} \pm \text{Crn.}
\]

On the high-pressure and low-temperature side, the Grt+CO$_2$ field is restricted by the reaction of the partial carbonation of garnet:

\[
\text{Grt} + 3\text{CO}_2 \rightarrow \text{Grt}_{\text{new}} + \text{CO}_2 + \text{Cal} + \text{Ky} + \text{Coe.}
\]

2. The addition of almandine to the Prp–Grs+CO$_2$ system shifts the limit of partial carbonation of garnet by 30–70 °C and the full carbonation of garnet by 100–140 °C below the Prp+CO$_2$ line. The Grt+CO$_2$ region appears at high temperatures and is continuous over the entire range of compositions. Along the Prp–Alm$_{50}$Grs$_{50}$ join, there is no garnet composition that would react with CO$_2$ to produce the Carb+Ky+Coe assemblage directly. The regions of Grt+CO$_2$ and Carb+Ky+Coe are separated by the Grt+CO$_2$+Carb+Ky+Coe field. The composition of garnet in the field of partial carbonation is richer in the almandine component than that in the Grt+CO$_2$ field.

3. In the eclogite–CO$_2$ system, the lower boundary of the Grt+Cpx+CO$_2$ assemblage almost coincides with the pyrope carbonation reaction. In the field of partial carbonation, the garnet and omphacite react with CO$_2$ to form carbonate, kyanite, coesite, garnet, and clinopyroxene with a new composition. Due to the carbonation of clinopyroxene, the temperature of the partial carbonation of eclogite is significantly higher than that of garnet, which restricts the eclogite + CO$_2$ stability field to pressures lower than the diamond stability field. The partial carbonation of the eclogite stabilizes the carbonate, kyanite, and coesite, wherein, the garnet composition shifts toward the garnet component, while the clinopyroxene composition evolves to jadeite. This would extend the CO$_2$ stability field in the eclogitic suite to lower temperatures. Yet, taking into account the fact that CO$_2$ is in short supply under natural conditions, it should be completely spent on the carbonation of the eclogite just below the eclogite + CO$_2$ field.

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Abbreviations
Ank ankerite
Alm almandine
Arg aragonite
Cal calcite
Carb carbonate
Coe coesite
Cpx clinopyroxene
Crn corundum
Di diopside
Dol dolomite
Ecl eclogite
Grs grossular
Grt garnet
Jd jadeite
Ky kyanite
Mgs magnesite
Qz quartz
Prp pyrope

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